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⑤④ Improvements in or relating to organic compounds.

⑤⑦ The invention relates to a method of controlling powdery mildew with a mixture of an EBI triazole fungicide and a dithiocarbamate fungicide employing an application rate of the EBI triazole fungicide allowing a reduction of the amount of dithiocarbamate to be applied and fungicidal compositions comprising such mixtures.

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The object of the present invention is an improved process for the control of downy mildew on plants.

Mildew (downy mildew in English literature) is a cryptogamic disease which is the cause of important devastation of plants, notable potatoes, tomatoes and especially the grapevine. The different fungi responsible for this disease belong to order of Oomycetes, such as *Plasmopara viticola* in the grapevine and *Phytophthora infestans* in potatoes and tomatoes. A certain number of products are available commercially for the control of downy mildew. Of these, the dithiocarbamate fungicides are generally used to control downy mildew, for example mancozeb at doses varying between 160 and 320 g/hl depending i.a. on the plants to be treated. However, their usage introduces disadvantages. Being preventive fungicides effective by contact, the efficiency of these compositions is limited by the fact that they are easily washed away by rain and that the plant parts formed after treatment are not protected, which means that it is necessary to renew the treatment and consequently to additionally supply active material which increases the cost of treatment and the risk of pollution of the environment. Whilst carrying out research in this field, the applicant has now surprisingly and unexpectedly found that ergosterol biosynthesis inhibiting fungicides (EBI fungicides) belonging to the triazole family enable a considerable reduction to be made in the dose of dithiocarbamate fungicide necessary to control downy mildew on plants, whilst remaining extremely effective. This is even more surprising given the fact that EBI fungicides, whilst allowing the control of rust and powdery mildew, are essentially ineffective against downy mildew on plants, which are Oomycetes fungi not synthesising sterols.

The invention therefore provides a method of controlling downy mildew on plants, which comprises treating the downy mildew, the plant to be protected or its locus with a downy mildew controlling aggregate amount of an ergosterol biosynthesis inhibiting (EBI) fungicide belonging to the class of triazoles [hereinafter called Component (b)] and a dithiocarbamate fungicide selected from zineb, maneb, mancozeb and propineb [hereinafter called Component (a)], characterised in that Component (a) is employed at an application rate which is below that necessary to control downy mildew when employed as sole active agent.

The amount of Component (b) to be employed to attain the desired effect is equal to or below the application rate necessary to control rust and/or powdery mildew on plants. The application rate of EBI triazole fungicide necessary to control rust and/or powdery mildew on plants is hereinafter designated Effective Application Rate.

Preferably Component (b) is employed at a rate which is lower than the Effective Application Rate.

The amount of EBI triazole fungicide and of dithiocarbamate fungicide to be applied depends on various factors, such as the components employed the type of treatment (plants, soil), the method of treatment (for example, spraying, dusting), the purpose of treatment (prophylactic or phytotherapeutic) and the period of application. In general, however, satisfactory results are obtained when applying to the downy mildew or the plants 0.005 to 0.100 kg, in particular 0.005 to 0.050, more in particular 0.005 to 0.030 kg, especially 0.005 to 0.020 kg, most preferably 0.005 to 0.015 kg of an EBI triazole fungicide (preferably cyproconazole) per hectare, together with 0.7 to 2.1 kg/ha, in particular 1.2 to 1.8 kg/ha, especially 1.3 and 1.6 kg/ha, more particularly 1.3 to 1.5 kg/ha of a dithiocarbamate fungicide (preferably mancozeb). According to a preferred embodiment, good result in controlling downy mildew on the grapevine are obtained when using 0.005 to 0.015 kg/ha, especially 0.01 kg/ha, of cyproconazole, together with 1.3 to 1.5 kg/ha, especially 1.4 kg/ha, of mancozeb.

Application of the EBI triazole fungicide and of the dithiocarbamate fungicide whether together or separately, may be effected according to known methods, assisted by conventional equipment. The compounds are preferably applied by spraying, generally employing a volume of application of between 0.05 and 15 hl per hectare, for example between 0.05 and 0.5 hl/ha for aerial application and between 2 and 15 hl/ha for customary (terrestrial or land) application.

In the present application, and in accordance with what is known from literature, an EBI triazole fungicide is understood to be a fungicide belonging to the class of triazoles which is active against rust and powdery mildew, for example by inhibiting C-14 demethylation of ergosterol biosynthesis in the fungi responsible for these diseases, but essentially inactive against downy mildew on plants. The application rate necessary to control rust and/or powdery mildew with an EBI triazole fungicide on plants is known. This Effective Application Rate varies according to the EBI fungicide used and is in general between 10 and 100 g/ha and may even be lower depending on the particular EBI fungicide employed. It may, for example be in the range of from 10 to 12 g/ha for cyproconazole for treatment of powdery mildew in the grapevine. According to the invention, the amount of Component (b) employed to achieve a potentiating effect on the fungicidal activity of Component (a) against downy mildew is conveniently equal to or lower than the Effective Application Rate; a potentiating effect is even observed when employing an amount of Component a) that is 50 % and more, even 75 % and more and most surprisingly even 85 % and more lower than the Effective Application Rate. For control of downy mildew on plants Component a) is, when applied without Component b) normally employed at application rates of from 2.5 and 3 kg/ha, notably 2.8 kg/ha. The EBI triazole fungicides according to the invention allow a net reduction in this dose for the control of downy mildew on plants. The rate reduction (of Component a) is substantial and can easily be 25 % or more especially more than 40 % and preferably 50 % or more.

Mixtures of an EBI triazole fungicide with mancozeb have already been proposed. Thus, a mixture of myclobutanil and mancozeb was proposed to control powdery mildew, black rot, downy mildew and parasitic rougeot of the grapevine. As with other known mixtures of mancozeb and EBI fungicides other than those belonging to the triazole family, the activity of this mixture against downy mildew is based solely on the normal rate of use of mancozeb that is employed (2.8 kg/ha), myclobutanil only being added to this latter at the normal rate of use to expand the spectrum of action of mancozeb with a view to controlling powdery mildew also. In all these mixtures, the EBI fungicide is not employed to reduce the dose of mancozeb necessary to control downy mildew and is not employed at a dose lower than the Effective Application Rate. A mixture of cyproconazole and mancozeb has similarly been proposed. However, such a mixture is intended to control only rust, powdery mildew and node canker of wheat, and not downy mildew of plants. In other respects, mancozeb is only used in this mixture to make up to the normal rate of use of cyproconazole to control cryptogamic diseases of wheat.

EBI triazole fungicides are known and their activity against rust and powdery mildew of plants is largely described in literature. Examples of EBI triazole fungicides which may be used according to the invention, are epoxyconazole, tetraconazole, bromiconazole, hexaconazole, flusilazol, etaconazole, tebuconazole, cyproconazole, difenoconazole, triadimefon, triadimenol, propiconazole, diclobutrazol, bitertanol, penconazole, flutriafol and diniconazole. The EBI triazole fungicide belonging to the triazole class is preferably hexaconazole or cyproconazole, more preferably cyproconazole. The dithiocarbamate fungicide is preferably mancozeb.

The invention also relates to the use of an EBI triazole fungicide (Component [b]) as a potentiator in a fungicidal composition containing a dithiocarbamate fungicide as defined above (Component [a]), an EBI triazole fungicide (Component [b]) and an agriculturally acceptable diluent for the control of downy mildew with a reduced amount of dithiocarbamate fungicide as defined above (Component [a]).

The term reduced amount of Component (a) as employed herein, refers to an amount lower than the amount of Component (a) effective to control downy mildew when applied as sole active ingredient.

The amount by which the amount of Component (a) effective to control downy mildew can be reduced when applied as sole active ingredient gives an indication of the potentiating effect of Component (b), since the latter shows when applied as sole active agent essentially no activity against downy mildew.

The invention also provides a fungicidal composition containing:

a) Component (a)

and

b) Component (b)

together with agriculturally acceptable diluents for the control of downy mildew characterised in that it contains a quantity of Component (b) capable of potentiating the fungicidal effect of Component (a) against downy mildew and that its volume to be applied per hectare contains less of Component (a) than the amount effective against downy mildew when applying Component (a) as sole active agent.

As indicated earlier, the content of Component (b) in the fungicide of the invention, will conveniently be selected such that its application rate will be equal to the Effective Application Rate (i.e. 10 to 100 g/ha) or lower. Though the content of Component (b) will depend i.a. on the particular EBI triazole fungicide employed, satisfactory potentiating effects will in general be obtained with contents of Component (b) corresponding with application rates in the range of from 5 to 100 g particularly of from 5 to 50 g of Component (b) per hectare.

The content of Component (a) in the fungicidal composition of the invention will conveniently be selected such that its volume to be applied per hectare (where desired after dilution with e.g. water) contains from 0.7 to 2.1 kg product.

Preferred fungicides of the invention contain mancozeb as Component (a).

Preferred Components (b) are selected from the azoles listed hereinabove, more preferably from hexaconazole and cyproconazole. The latter is particularly preferred.

In the mixture according to the invention, the weight ratio of the EBI triazole fungicide to the dithiocarbamate fungicide as specified above, is advantageously between 1:420 and 1:14, in particular between 1:360 and 1:40, especially between 1:320 and 1:65 and more particularly between 1:300 and 3:260 (i.e. ca. 1:87). A suitable weight ratio is for example 1:130 to 150, notable 1:140.

In general it is particularly advantageous to employ at least 110 parts by weight of dithiocarbamate fungicide together with 1 part by weight of EBI triazole fungicide. The mixture, as defined above, of components a) and b) is notable for its remarkable fungicidal activity against downy mildew of plants. In particular, such a mixture has proved to be effective to control downy mildew of the grapevine, the potato, tobacco, ornamental plants and market-garden produce, such as tomatoes, peas, lettuce, etc., especially downy mildew of the grapevine. On the grapevine, such a mixture possesses moreover fungicidal activity against powdery mildew and other secondary diseases of the grapevine, such as black rot and parasitic rougeot. The mixture of Components a) and b) as defined above is thus particularly suitable for the control of downy mildew in plants such as the grapevine, potatoes, tobacco, tomatoes and other solanacea, citrus fruit, strawberries, vegetables and ornamental

plants, for example for the control of fungi of the genus *Plasmopara*, for example *Plasmopara viticola* in the grapevine, the genus *Phytophthora*, for example *Phytophthora infestans* in the cultivation of potatoes, tomatoes and other Solanaceae, *Phytophthora parasitica* in the cultivation of tomatoes and other Solanaceae, *Phytophthora cryptogaea* in the cultivation of tomatoes and other Solanaceae, and *Phytophthora cactorum* and *Phytophthora fragariae* in the cultivation of strawberries, the genus *Bremia*, for example *Bremia lactucae* in plants such as lettuce, the genus *Peronospora*, for example *Peronospora tabacina* in tobacco, as well as the control of fungi of the genus *Guignardia*, for example *Guignardia bidwellii* in the grapevine, the genus *Pseudopeziza*, for example *Pseudopeziza tracheiphila* in the grapevine, and the genus *Botrytis* in the grapevine and in lettuce, for example *Botrytis cinerea* in the grapevine.

The mixture of Components a) and b) as described above, is preferably used to control downy mildew of the grapevine.

According to a preferred embodiment, the invention relates to the use of a mixture comprising cyproconazole and mancozeb, in the weight ratios mentioned above, to control downy mildew of the grapevine. Such a mixture allows downy mildew of the grapevine to be controlled with doses of mancozeb as weak as 1.4 kg/ha instead of 2.8 kg/ha.

The fungicidal compositions of the invention may exist in solid or liquid form, for example in the form of wettable powder, as a concentrated suspension which is dispersible in water, as a powder for dusting, as a granule, or as a composition having delayed release, containing the usual diluents, and they may be prepared according to known methods, for example by mixing the active materials with a diluent and eventually with other formulation agents such as surfactants.

The diluents are understood to be liquid or solid products which are acceptable in agriculture, capable of being added to active materials so as to put them in a form of application which is simpler or improved, or to enable them to be used at the desired concentration. They may be for example talc, kaolin, diatomaceous earth, polyglycol or water.

The composition intended for spraying, such as concentrates which are dispersible in water or wettable powders, may contain surfactants such as wetting agents and dispersants, for example the product of condensation of formaldehyde with a naphthalene sulphonate, an alkylaryl sulphonate, a lignin sulphonate, a fatty alcohol sulphate, an ethoxylated alkylphenol and an ethoxylated fatty alcohol.

In general, the fungicidal compositions consist of 0.01 to 90 % by weight of active material, 0 to 20 % by weight of surfactant which is acceptable in agriculture and 99.99 to 20 % by weight of one or several solid or liquid diluents, the active material being in the proportions indicated above. The concentrated forms generally contain between about 2 to 90 %, preferably between about 5 and 70 % by weight of active materials. The forms which are ready for use may contain for example 0.01 to 45 % by weight, preferably 0.01 to 5 % by weight of active material.

Examples of suitable application forms of the fungicidal compositions of the invention contain from 0.7 to 2.1 kg of Component (a) in 1000 liter spray liquor.

In addition to the usual diluents and surfactants, the compositions may contain other additives having specific effects, for example stabilizers, agents which improve adhesion to plants, corrosion inhibitors, anti-foaming agents and colourants. In the following examples, which illustrate the invention without limiting its scope in any way, the parts are by weight.

**EXAMPLE 1****Wettable Powder****5    Composition in %**

	techn. cyproconazole	
	(with 91 % active material)	0.55
10	techn. mancozeb	
	(with 85 % active material)	83.00
	dispersant <sup>1)</sup>	6.00
15	wetting agent <sup>2)</sup>	1.45
	filler <sup>3)</sup>	9.00
	<b>total</b>	<hr/> 100.00

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1) for example sodium or calcium lignosulphonate or sodium  
25 polynaphthalene sulphonate

2) for example nonylphenol or sodium lauryl sulphate

30 3) for example kaolin, colloidal silicon dioxide or talc.

All the components are mixed and they are ground until obtaining particles having an average dimension of  
35 between 2 and 5 microns.

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**EXAMPLE 2****Wettable granules****5    Composition in %**

	techn. cyproconazole	
	(with 91 % active material)	0.55
10	techn. mancozeb	
	(with 85 % active material)	83.00
	dispersant <sup>1)</sup>	15.45
15	wetting agent <sup>2)</sup>	1.00
		<hr/>
20	<b>total</b>	<b>100.00</b>

25    <sup>1)</sup>    for example sodium lignosulphonate or sodium polynaphthalene  
sulphonate

30    <sup>2)</sup>    for example sodium isopropyl naphthalene sulphonate or sodium  
lauryl sulphate.

35    All the components are mixed with water so as to obtain a paste, which is ground in a ball mill until the  
particles have a dimension of between 1 and 5 microns. The paste obtained is then dried and it is transformed  
by known methods in wettable granules.

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**EXAMPLE 3****Concentrated suspension**5 **Composition in %**

	techn. cyproconazole	
	(with 91 % active material)	0.25
10	techn. mancozeb	
	(with 85 % active material)	37.80
	dispersant <sup>1)</sup>	5.00
15	softening agent <sup>2)</sup>	1.00
	antigel <sup>3)</sup>	6.00
	thickener	0.30
20	water	49.65
	<b>total</b>	<b>100.00</b>

25 <sup>1)</sup> for example sodium lignosulphonate or sodium polynaphthalene  
sulphonate

30 <sup>2)</sup> for example nonylphenol or a sodium alkyl naphthalene sulphonate

35 <sup>3)</sup> for example ethylene glycol or propylene glycol.

All the components are mixed with water so as to obtain a paste which is ground using a ball mill until the dimension of the particles is between 1 and 5 microns.

40 **EXAMPLE 4**

In the formulation of Examples 1 to 3 above, cyproconazole is replaced by any one of the EBI triazole fungicides mentioned in the description.

45 **EXAMPLE 5**

In the preceding Examples 1 to 4, mancozeb is replaced by zineb, maneb, mancopper or propineb.

50 **EXAMPLE 6**

The efficiency of the mixture according to the invention in controlling downy mildew has been demonstrated in tests made on vine plots. In these tests, an aqueous composition formulated according to Example 1 or 2, and containing per 100 litres, 1 g of cyproconazole and 140 g of mancozeb, is applied by spraying. The composition is applied at doses ranging from 600 to 1300 l/ha and at different stages of development of the vine, from the 6-7 leaf stage until ripening. After application, the average rate of attack on leaves and on grapes is determined as %. Effective action against downy mildew is observed, the average rate of attack of the treated plants being generally less than 25 % of leaves and less than 20 % of grapes, whilst untreated control plants

have a rate of attack of 98 % on leaves and 90 % on grapes. In these tests, the mixture has an activity which is markedly superior to the activity of each of the constituents when taken individually.

Satisfactory results are similarly obtained with the compositions of Examples 3 to 5.

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## Claims

1. A method of controlling downy mildew on plants, which comprises treating the downy mildew, the plant to be protected or its locus with a downy mildew controlling aggregate amount of an ergosterol biosynthesis inhibiting (EBI) fungicide belonging to the class of triazoles [hereinafter called Component (b)] and a dithiocarbamate fungicide selected from zineb, maneb, mancooper, mancozeb and propineb [hereinafter called Component (a)], characterised in that Component (a) is employed at an application rate below that necessary to control downy mildew when employed as sole active agent.
2. The method of Claim 1, wherein Component (b) is applied at a rate of from 5 g to 50 g/ha.
3. The method of Claim 2, wherein Component (a) is applied at a rate of from 0.7 to 2.1 kg/ha.
4. The method of Claims 1 to 3, wherein Component (b) is selected from epoxyconazole, tetraconazole, bromiconazole, hexaconazole, flusilazol, etaconazole, tebuconazole, cyproconazole, difenoconazole, triadimefon, triadimenol, propiconazole, diclobutrazol, bitertanol, penconazole, flutriafol and diniconazole.
5. The method of Claims 1 to 4, wherein Component (b) is selected from hexaconazole, flusilazol, etaconazole, tebuconazole, cyproconazole, difenoconazole, triadimefon, triadimenol, propiconazole, diclobutrazol, bitertanol, penconazole, flutriafol and diniconazole.
6. The method of Claims 1 to 5, wherein Component (b) is hexaconazole or cyproconazole.
7. The method of Claims 1 to 6, wherein Component (b) is cyproconazole.
8. The method of Claims 1 to 7, wherein Component (a) is mancozeb.
9. A fungicidal composition containing
  - a) an EBI triazole fungicide
  - and
  - b) a dithiocarbamate fungicide selected from zineb, maneb, mancooper, mancozeb and propineb together with agriculturally acceptable diluents for the control of downy mildew characterised in that it contains a quantity of Component (b) capable of potentiating the fungicidal effect of Component (a) against downy mildew and that its volume to be applied per hectare contains less of Component (a) than the amount effective against downy mildew when applying Component (a) as sole active agent.
10. The fungicide of Claim 9, containing from 0.7 to 2.1 kg of Component (a) in the volume to be applied per hectare.
11. The fungicide according to Claims 9 or 10, wherein the weight ratio of Component (a): Component (b) is in the range of from 1:420 to 1:14.
12. The fungicide according to Claims 10 or 11, wherein the weight ratio of Component (a): Component (b) is in the range of from 1:360 to 1:40.
13. The fungicide according to Claim 12, wherein the weight ratio of Component (a): Component (b) is in the range of from 1:320 to 1:65.
14. The fungicide according to Claim 13, wherein the weight ratio of Component (a): Component (b) is in the range of from 1:300 to 3:260.
15. The fungicide of Claims 9 to 14 comprising at least 110 parts by weight of Component (a) for one part by weight of Component (b).
16. The fungicide of Claim 15, wherein the weight ratio of Component (a): Component (b) is in the range of



from 1:130 to 1:150.

17. The fungicide of Claims 9 to 16, wherein Component (b) is selected from epoxyconazole, tetraconazole, bromiconazole, hexaconazole, flusilazol, etaconazole, tebuconazole, cyproconazole, difenoconazole, triadimefon, triadimenol, propiconazole, diclobutrazol, bitertanol, penconazole, flutriafol and diniconazole.
18. The fungicide of Claim 17, wherein Component (b) is selected from hexaconazole, flusilazol, etaconazole, tebuconazole, cyproconazole, difenoconazole, triadimefon, triadimenol, propiconazole, diclobutrazol, bitertanol, penconazole, flutriafol and diniconazole.
19. The fungicide of Claim 18, wherein Component (b) is hexaconazole or cyproconazole.
20. The fungicide of Claim 19, wherein Component (b) is cyproconazole.
21. The fungicide of Claims 9 to 20, wherein Component (a) is mancozeb.
22. The use of an EBI triazole fungicide as a potentiator in a fungicidal composition containing a dithiocarbamate fungicide selected from zineb, maneb, mancopper, mancozeb and propineb, an EBI triazole fungicide and an agriculturally acceptable diluent for the control of downy mildew with a reduced amount of dithiocarbamate fungicide per hectare.
23. A fungicidal composition containing:
  - a) an EBI triazole fungicide
  - and
  - b) a dithiocarbamate fungicide selected from zineb, maneb, mancopper, mancozeb and propineb together with agriculturally acceptable diluents, characterised in that it contains at least 110 parts by weight of Component (a) for one part by weight of Component (b).



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
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X	EP-A-0 316 970 (BAYER AG) * page 2, line 9 - page 3, line 19 * * page 6, line 49 - page 6, line 52 * * page 7, line 8 - page 7, line 32; claims *	1-23	
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Place of search THE HAGUE		Date of completion of the search 29 JULY 1992	Examiner DONOVAN T. M.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

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X	<p>--- DE-A-3 333 449 (BAYER AG) * page 11, line 1 - page 13, line 5 * * page 23, line 28 - page 24, line 8; claims; example C *</p> <p>--- -/--</p>	9-16,23		
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Place of search THE HAGUE		Date of completion of the search 29 JULY 1992	Examiner DONOVAN T.M.	
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>				

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PHYTOPROTECTION vol. 71, 1990, QUEBEC, CANADA pages 1 - 8; J. WARNER: 'Field comparison of sterol-biosynthesis-inhibiting fungicides used alone and in combination with protectant fungicides for apple scab control' * page 3 - page 7 * ---	9-21, 23	
X	PHYTOPROTECTION vol. 71, 1990, QUEBEC, CANADA pages 9 - 15; A. R. BIGGS & J. WARNER: 'Full-season and post-harvest applications of sterol-inhibiting fungicides to reduce ascospore formation in Venturia inaequalis' * page 11 - page 14 * -----	9-19, 21, 23	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 JULY 1992	Examiner DONOVAN T. M.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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